

| | Type | L # | Hits | Search Text | DBs | Time Stamp |
|---|------|-----|------|--|--|------------------|
| 1 | BRS | L2 | 2 | ("gas phase" or "gas-phase") with oxidat? | USPAT; US-PGP UB; EPO; JPO; DERWENT | 2004/09/28 16:25 |
| 2 | BRS | L3 | 4 | ("gas phase" or "gas-phase" or "vapor phase" or "vapor phase") with oxidat? | USPAT; US-PGP UB; EPO; JPO; DERWENT | 2004/09/28 16:25 |
| 3 | BRS | L4 | 7882 | ("gas phase" or "gas-phase" or "vapor phase" or "vapor phase") with oxidat\$ | USPAT; US-PGP UB; EPO; JPO; DERWENT | 2004/09/28 16:25 |
| 4 | BRS | L5 | 2 | 14 and "radial compressor" | USPAT; US-PGP UB; EPO; JPO; DERWENT | 2004/09/28 16:26 |
| 5 | BRS | L6 | 263 | 14 and compressor | USPAT; US-PGP UB; EPO; JPO; DERWENT | 2004/09/28 16:30 |
| 6 | BRS | L7 | 263 | 14 and (compressor or compressor) | USPAT; US-PGP UB; EPO; JPO; DERWENT | 2004/09/28 16:31 |

| | Comments | Error Definition | Errors |
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| 1 | | | 0 |
| 2 | | | 0 |
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| 7 | BRS | L8 | 65 | 17 and (acrylic or methacrylic or (meth)acrylic) | USPAT; US-PGP UB; EPO; JPO; DERWEN T | 2004/09/28 16:33 |
| 8 | BRS | L9 | 6 | 17 and ammox\$ | USPAT; US-PGP UB; EPO; JPO; DERWEN T | 2004/09/28 16:38 |
| 9 | BRS | L10 | 21 | 17 and (propane with acrylic) | USPAT; US-PGP UB; EPO; JPO; DERWEN T | 2004/09/28 16:43 |
| 10 | BRS | L11 | 1 | "10259023" | EPO; DERWEN T | 2004/09/28 16:44 |
| 11 | BRS | L12 | 1 | "20040116730" | EPO; DERWEN T | 2004/09/28 16:45 |
| 12 | BRS | L13 | 21655 | 4,077,912 4,105,744 3,956,377 4,496,770 4,408,079 5,264,625 5,231,226 5,173,468 5,221 ,767 3,799,886 3,119,837 3,702,259 5,734,068 5,668,077 | USPAT | 2004/09/28 16:46 |
| 13 | BRS | L14 | 14 | US-4077912-\$ DID. OR US-4105744-\$ DID. OR US-3956377-\$ DID. OR US-4496770-\$ DID. OR US-4408079-\$ DID. OR US-5264625-\$ DID. OR US-5231226-\$ DID. OR US-5173468-\$ DID. OR US-5221767-\$ DID. OR US-3799886-\$ DID. OR US-3119837-\$ DID. OR US-3702259-\$ DID. OR US-5734068-\$ DID. OR US-5668077-\$ DID. | USPAT | 2004/09/28 16:48 |

| | Comments | Error Definition | Errors |
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| 7 | | | 0 |
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| 9 | | | 0 |
| 10 | | | 0 |
| 11 | | | 0 |
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| | Type | L # | Hits | Search Text | DBs | Time Stamp |
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| 14 | BRS | L15 | 5 | US-6410785-\$ DID. OR US-5637222-\$ DID. OR US-6348638-\$ DID. OR US-6395936-\$ DID. OR US-6403829-\$ DID. OR US-6395936-\$ DID. | USPAT | 2004/09/28 16:51 |
| 15 | BRS | L16 | 0 | "2003018729" | US-PGP UB | 2004/09/28 17:15 |
| 16 | BRS | L17 | 1 | 6433222.pn. | USPAT | 2004/09/28 17:28 |
| 17 | BRS | L18 | 1 | 5245093.pn. | USPAT | 2004/09/28 17:28 |

| | Comments | Error Definition | Errors |
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| 14 | | | 0 |
| 15 | | | 0 |
| 16 | | | 0 |
| 17 | | | 0 |



US006433222B1

(12) **United States Patent**
Eck et al.

(10) Patent No.: US 6,433,222 B1

(45) Date of Patent: Aug. 13, 2002

(54) METHOD FOR PRODUCING ACRYLIC ACID

EP 0 117 146 8/1984

8/1984

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10-667782

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(21) Appl. No.: 09/764,985

(22) PCT Filed: Jul 21, 1999

(86) PCT №.: PCT/EP99/05204

§ 371 (c)(1),
(2), (4) Date: Jan. 22, 2001

(87) PCT Pub. No.: WO00/05188

PCT Pub. Date: Feb. 3, 2000

30) **Foreign Application Priority Data**

Jul. 22, 1998 (DE) 198 33 049
(51) Int. Cl.⁷ C07C 51/42
(52) U.S. Cl. 562/600; 562/600; 562/545
(58) Field of Search 562/600; 545

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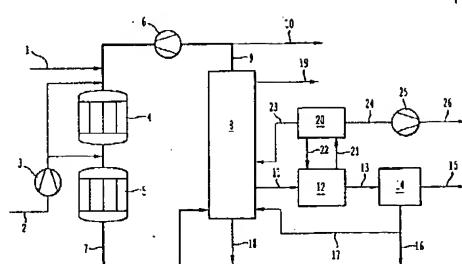
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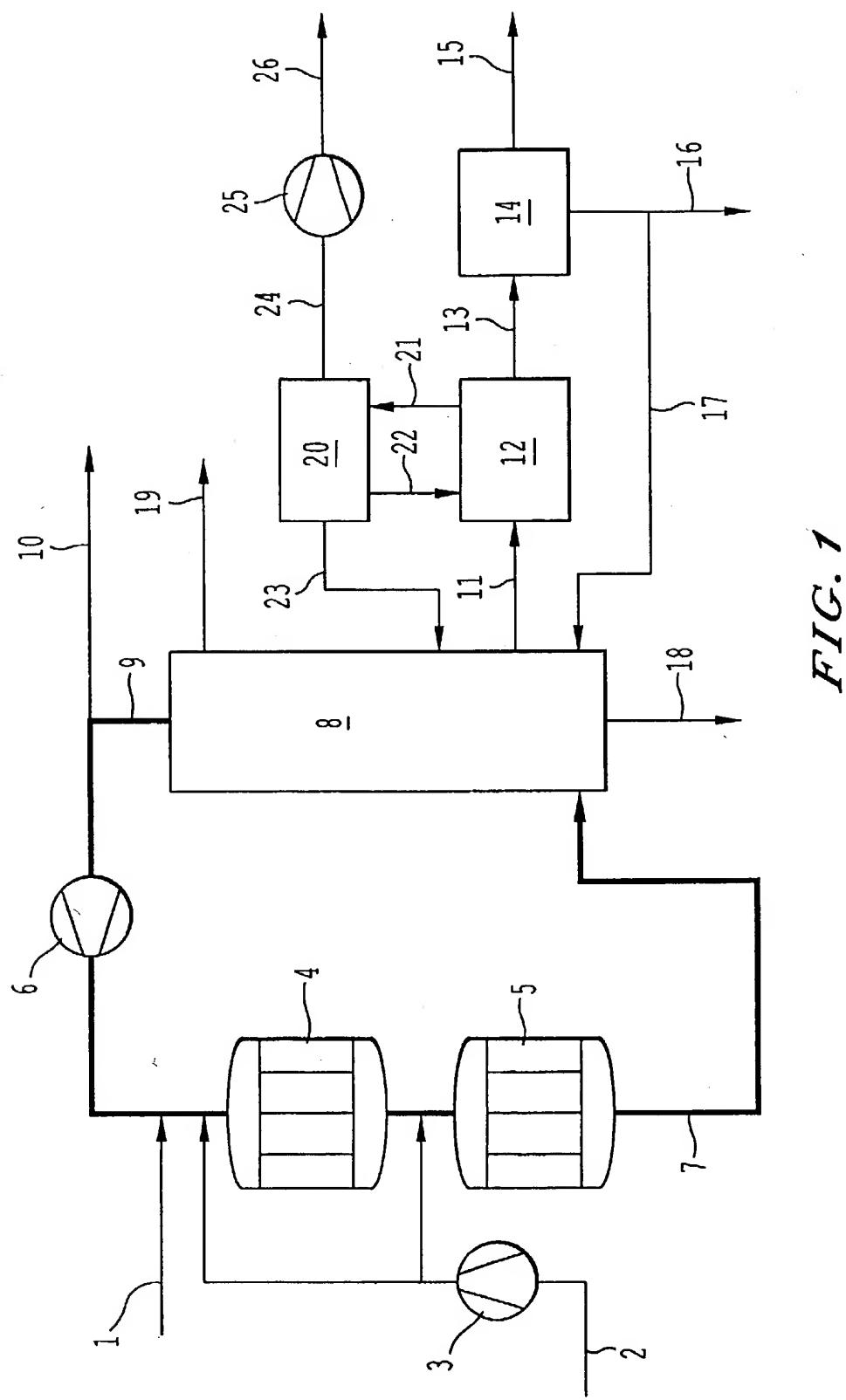
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20 Claims, 1 Drawing Sheet





METHOD FOR PRODUCING ACRYLIC ACID

The present invention relates to a process for the preparation of acrylic acid.

Acrylic acid is an important key chemical. Owing to its very reactive double bond and the acid function, it is particularly suitable as a monomer for the preparation of polymers. Of the amount of acrylic acid monomers produced, the major part is esterified before the polymerization—to give, for example, adhesives, dispersions or surface coatings. Only the minor part of the acrylic acid monomers produced is polymerized directly—to give, for example, "superabsorbers". Whereas monomers of high purity are generally required in the direct polymerization of acrylic acid, the requirements regarding the purity of acrylic acid are not so high when they are esterified before the polymerization.

It is generally known that acrylic acid can be prepared by gas-phase oxidation of propene with molecular oxygen under heterogeneous catalysis over catalysts present in the solid state at from 200 to 400° C. in one stage or two stages via acrolein (cf. for example DE-A-1 962 431, DE-A-2 943 707, DE-C-1 205 502, DE-A-195 08 558, EP-A-0 257 565, EP-A-0 253 409, DE-A-2 251 364, EP-A-0 117 146, GB-B-1 450 986 and EP-A-0 293 224). Here, oxidic multicomponent catalysts, for example based on oxides of the elements molybdenum, bismuth and iron (in the 1st stage) or molybdenum and vanadium (in the 2nd stage) are used.

DE-C-2 136 396 discloses the separation of the acrylic acid from the reaction gases obtained in the catalytic oxidation of propene or acrolein by countercurrent absorption with a mixture of about 75% by weight of diphenyl ether and about 25% by weight of biphenyl. Furthermore, DE-A-2 449 780 discloses the cooling of the hot reaction gas by partial evaporation of the solvent in a direct condenser (quench apparatus) before the countercurrent absorption. What is problematic here and in further process steps is that solids are obtained in the apparatuses, reducing the availability of the plant. According to DE-A-4 308 087, the production of these solids can be reduced by adding a polar solvent, such as dimethyl phthalate in an amount of from 0.1 to 25% by weight to the relatively nonpolar solvent mixture comprising diphenyl ether and biphenyl.

In addition to the absorption, described above, of the acrylic acid-containing reaction product into a high-boiling solvent mixture, other known processes provide total condensation of acrylic acid and of the water of reaction furthermore formed in the catalytic oxidation. This gives an aqueous acrylic acid solution which can be further worked up by distillation with an azeotropic agent (cf. DE-C-3 429 391, JP-A-1 124 766, JP-A-7 118 766, JP-A-7 118 966-R, JP-A-7 118 968-R, JP-A-7 241 885) or by an extraction method (cf. DE-A-2 164 767, JP-A-5 81 40-039 and JP-A-4 80 91 013). In EP-A-0 551 111 the mixture of acrylic acid and byproducts which is prepared by means of catalytic gas-phase oxidation is brought into contact with water in an absorption tower, and the resulting aqueous solution is distilled in the presence of a solvent which forms an azeotropic mixture with polar low boilers, such as water or acetic acid. DE-C-2 323 328 describes the separation of acrylic acid from an aqueous butanol/acrylic acid esterification waste liquor by extraction with a special mixture of organic solvents.

The disadvantage of the processes described above is that the organic solvent used for the extraction or absorption is separated off again in a further process stage, such as a rectification under high thermal stress. This gives rise to the danger of polymerization of the acrylic acid.

JP-A-07 082 210 describes a process for purifying acrylic acid which, in addition to acrylic acid contains acetic acid, propionic acid, acrolein and furfural. In this process, a crystallization is carried out under reduced pressure after the addition of water, a purity of 99.6% being achieved after isolation and washing of the acrylic acid crystals. Japanese Patent 45-32417 discloses a process in which an aqueous acrylic acid solution which additionally contains acetic acid and propionic acid is extracted with heptane or toluene, and water is then removed from the extract by distillation. In the next stage, the remaining extract is cooled to -20 to -80° C. in order to induce crystallization of acrylic acid. The crystals are isolated and the mother liquor is recycled to the extraction process. According to this patent, the use of an organic solvent or extracting agent is necessary since otherwise the solution, if it is cooled, solidifies without crystals being precipitated. The disadvantage of this process, apart from the addition of an organic solvent, is that a distillation has to be carried out to separate off water. Canadian Patent 790 625 relates to a further purification process of crude acrylic acid by fractional crystallization. There, the temperature is not reduced below the peritectic temperature of the acrylic acid/propionic acid system where propionic acid is the main impurity in the crude acrylic acid, while the temperature is not reduced below the eutectic temperature of the acrylic acid/acetic acid system where acetic acid is the main impurity. The acrylic acid used for crystallization is prepared here by conventional processes, for example by gas-phase oxidation of propene or acrolein, and then subjected to a preliminary purification by conventional known methods, e.g. extraction. According to the patent, the crystallization of the acrylic acid is preferably carried out essentially in the absence of water.

EP-A-0 616 998 describes a process for purifying acrylic acid by means of a combination of dynamic and static crystallization, the starting material used being prepurified acrylic acid, for example acrylic acid prepurified by distillation.

The common feature of the processes described in the above documents is that they require a preliminary purification of the acrylic acid before the crystallization. Since organic solvents are generally used in the preliminary purification and are subsequently separated off again under high thermal stress, the problem of undesired polymerization of the acrylic acid is always present here.

EP-A-0 002 612, which relates to a process for purifying acrylic acid present in aqueous solution by fractional crystallization, discloses the addition of salts to the acrylic acid solution in order to break the water/acrylic acid eutectic mixture which contains 63% by volume of acrylic acid.

EP-A-0 675 100 describes a process for the preparation of α,β -unsaturated C_3-C_6 -carboxylic acids, e.g. acrylic acid, by oxidative dehydrogenation of the corresponding saturated C_3-C_6 -carboxylic acid followed by crystallization of the melt with subsequent fractional distillation or followed by fractional distillation with subsequent crystallization of the melt. It is an object of the present invention to provide a process from which acrylic acid is obtained in high purity without expensive process stages.

We have found that this object is achieved and that, surprisingly, acrylic acid from a gaseous product mixture which is subjected to a condensation can be crystallized directly from the solution formed in the condensation. We have found in particular that no further purification stage and no addition of assistants are required for this purpose.

The present invention therefore relates to a process for the preparation of acrylic acid by:

- (a) preparation of a gaseous product mixture which essentially has the composition of a reaction mixture of catalytic gas-phase oxidation of C_3 -alkanes, C_3 -alkenes, C_3 -alkanols and/or C_3 -alkanals and/or precursors thereof to acrylic acid, which comprises
- (b) condensation of the gaseous product mixture,
- (c) crystallization of the acrylic acid from the solution obtained in stage (b), with partial evaporation of the solution under reduced pressure,
- (d) isolation of the resulting crystals from the mother liquor,
- (e) recycling of at least a part of the mother liquor from stage (d) to stage (b) and
- (f) recycling of at least a part of the evaporated solution from stage (c) to stage (b).

In a preferred embodiment, the condensation in stage (b) is carried out in a column. Further preferred embodiments of the invention are evident from the following description, the subclaims, the figure and the example.

In the novel process, the acrylic acid is crystallized directly, without further intermediate or purification stages and without the addition of assistants, from the solution formed in the condensation of the product mixture. This product mixture essentially has the composition of reaction product formed in the catalytic gas-phase oxidation to give the acid.

The single figure shows a preferred embodiment for carrying out the novel process.

Here, the terms high boiler, medium boiler and low boiler and corresponding adjectival terms denote compounds/substances which have a boiling point higher than that of acrylic acid (high boilers) or those which have a boiling point which is roughly the same as that of acrylic acid (medium boilers) or those which have a boiling point lower than that of acrylic acid (low boilers).

Stage (a)

A gaseous-product mixture which essentially has the composition of a reaction mixture of the catalytic gas-phase oxidation of C_3 -alkanes, C_3 -alkenes, C_3 -alkanols and/or C_3 -alkanals and/or precursors thereof to acrylic acid is prepared in stage (a). Particularly advantageously, the gaseous product mixture is prepared by catalytic gas-phase oxidation of propene, propane or acrolein. All precursors of the abovementioned C_3 compounds in which the actual C_3 starting compound is formed as a precursor only during the gas-phase oxidation can be used as starting compounds. Acrylic acid can be prepared directly from propane.

The catalytic gas-phase reaction of propene and/or acrolein with molecular oxygen to give acrylic acid by known processes, in particular as described in the abovementioned publications, is particularly advantageous. Here, temperatures of from 200 to 450° C. and, if required, superatmospheric pressure are preferably employed. Preferably used heterogeneous catalysts are oxidic multicomponent catalysts based on the oxides of molybdenum, bismuth and iron in the 1st stage (oxidation of propene to acrolein) and on the oxides of molybdenum and vanadium in the 2nd stage (oxidation of acrolein to acrylic acid). These reactions are carried out, for example, in one stage or two stages. If the starting material used is propane, it can be converted into a propene/propane mixture by: catalytic oxydehydrogenation as described, for example, in *Catalysis Today* 24 (1995), 307-313 or U.S. Pat. No. 5,510,558; by homogeneous oxydehydrogenation, as described, for example, in CN-A-1 105 352; or by catalytic dehydrogenation, as described, for

example, in EP-A-0 253 409, DE-A-195 08 558, EP-A-0 293 224 or EP-A-0 117 146. Suitable propene/propane mixtures are also refinery propene (70% of propene and 30% of propane) or cracker propene (95% of propene and 5% of propane). In principle, propene/propane mixtures such as the abovementioned ones can be oxidized with oxygen or air or a mixture of oxygen and nitrogen of any composition to give acrolein and acrylic acid. When a propene/propane mixture is used, propane acts as a diluent gas and/or reactant. A suitable process is also described in EP-B-0 608 838, in which propane as a reactant is converted directly into acrylic acid.

The conversion of propene into acrylic acid is highly exothermic. The reaction gas, which, in addition to the starting materials and products advantageously contains an inert diluent gas, e.g. circulating gas, atmospheric nitrogen, one or more saturated C_1 - C_6 -hydrocarbons, in particular methane and/or propane, and/or steam, can therefore absorb only a small part of the heat of reaction. Although the type of reactors used is not subject to any restriction per se, tube-bundle heat exchangers which are filled with the oxidation catalyst are generally used since, in said heat exchangers, the predominant part of the heat evolved in the reaction can be removed by convection and radiation to the cooled tube walls.

In the catalytic gas-phase oxidation, a gaseous mixture which, in addition to the acrylic acid, may contain essentially unconverted acrolein and/or propene, steam, carbon monoxide, carbon dioxide, nitrogen, propane, oxygen, acetic acid, propionic acid, formaldehyde, further aldehydes and maleic anhydride as byproducts is obtained instead of pure acrylic acid. Usually, the reaction product mixture contains from 1 to 30% by weight of acrylic acid, from 0.05 to 1% by weight of propene and from 0.05 to 1% by weight of acrolein, from 50 to 98% by weight of inert diluent gases, from 0.05 to 10% by weight of oxygen, from 0.05 to 2% by weight of acetic acid, from 0.01 to 2% by weight of propionic acid, from 0.05 to 1% by weight of formaldehyde, from 0.05 to 2% by weight of aldehydes and from 0.01 to 0.5% by weight of maleic anhydride, based in each case on the total reaction mixture. In particular, saturated C_1 - C_6 -hydrocarbons, such as from 0 to 90% by weight of methane and/or propane, as well as from 1 to 30% by weight of steam, from 0.05 to 15% by weight of carbon oxides and from 0 to 90% by weight of nitrogen, based in each case on 100% by weight of diluent gas, are contained as inert diluent gases.

Stage (b)

In stage (b), the reaction product obtained in stage (a) is subjected to a condensation, in particular a partial or total condensation, a solution being obtained.

The condensation is preferably carried out in a column. Here, a column having baffles which effect separation, in particular having packings and/or trays, preferably bubble trays, sieve trays, valve trays and/or dual-flow trays, is used. The condensable components of the gaseous product mixture from stage (a) are condensed as fractions by cooling. Since, owing to the impurities and diluent gases, the gas mixture contains a high boiler, medium boiler and low boiler fraction and uncondensable components, one or more side take-offs can be provided at the appropriate points in the column. In contrast to a conventional condensation, a condensation in a column thus permits separation into the individual components. Suitable columns comprise at least one cooling apparatus, for which all conventional heat transfer apparatuses or heat exchangers in which the heat

formed in the condensation is removed indirectly (externally) are suitable. Tube-bundle heat exchangers, plate-type heat exchangers and air coolers are preferred. Suitable cooling media are air in the corresponding air coolers and cooling liquids, in particular water, in other cooling apparatuses. If only one cooling apparatus is provided, it is installed at the top of the column in which the low boiler fraction is condensed. Since the acrylic acid-containing gas mixture contains plurality of fractions, it is expedient to install a plurality of cooling apparatuses in various sections of the column, for example a cooling apparatus in the lower section of the column for condensing the high boiler fraction and a cooling apparatus at the top of the column for condensing the low boiler fraction. The fraction containing the acrylic acid is removed in the middle part of the column, via one or more side take-offs. The pressure present in the column depends on the amount of uncondensable components and is preferably 0.5-5, in particular 0.8-3, bar absolute pressure. The exact operating conditions for the column, such as temperature and pressure, connection and arrangement of the cooling apparatus(es), arrangement of the side take-off/side take-offs for removing acrylic acid, choice of the column height and of the column diameter, number and spacing of the baffles/trays effecting separation in the column or type of column baffles effecting separation, can be determined by a person skilled in the art in experiments customary in the field, depending on the separation task. In a preferred embodiment, the hot gas mixture is cooled directly or indirectly before the condensation. In the case of direct cooling, it is preferable if the gas mixture is cooled with the aid of the high boiler fraction condensed from the gas mixture. In another case, an assistant is introduced into the process but has to be worked up again. In terms of apparatus, this preliminary cooling can be integrated in the bottom region of the column (with or without column baffles) or can be separated from the column in a separate apparatus, for example a gas cooler, a quench apparatus or a flash pot. In a particularly preferred embodiment of the invention, the condensation of the gaseous reaction mixture takes place in a column as follows, it being possible to organize the column in various sections in which the following different process functions are performed:

1. Bottom region: Cooling of the hot gas mixture

The hot gas mixture is passed into the bottom region and cooled. This can be effected by indirect cooling, for example by means of a heat exchanger, or by direct cooling with, as the cooling medium, high boiler fraction condensed in the next section of the column.

2. First cooling loop: Condensation of the high boiler fraction

In the region of the first cooling loop, the heat of condensation is removed externally via the first cooling loop by means of a heat exchanger with, for example, water as cooling medium, by removing condensed high boiler fraction from the column, cooling said fraction by means of the heat exchanger and recycling a part of the cooled, condensed, high boiler fraction to the column while the other part, usually less than 1% by weight, based on 100% by weight of condensate, in a side take-off, is removed. The recycled, condensed high boiler fraction is fed countercurrent to the ascending gas.

3. First cooling loop to side take-off: High boiler concentration

Between the first cooling loop and the side take-off, distillative concentration and condensation of the high

boiler fraction from the gas stream fed countercurrent upward are effected toward the first cooling loop.

4. Side take-off Removal of the acid

Acrylic acid is removed via the side take-off.

5. Side take-off to second cooling loop Concentration of the medium boiler fraction

In the region between the side take-off and the second cooling loop, the medium boiler fraction from the gas stream fed countercurrent upward is concentrated, the medium boiler fraction being concentrated toward the side take-off.

6. Second cooling loop Condensation of the low boiler fraction

In the region of the second cooling loop, the low boiler fraction from the gas stream fed countercurrent upward is condensed. The heat of condensation is removed externally via the second cooling loop by means of a heat exchanger with, for example, water as cooling medium, by removing condensed low boiler fraction and cooling it and recycling a part of the cooled, condensed low boiler fraction to the column while the other part is removed. The uncondensed components, which are preferably nitrogen, carbon monoxide, carbon dioxide, oxygen, methane, propane and propene, are removed from the top of the column.

In addition, the condensation can be carried out by conventional methods in one stage or a plurality of stages, the type of condensation not being subject to any particular restriction. Advantageously, the condensation is carried out using a direct condenser, condensate already produced being brought into contact with the hot gaseous reaction product. Suitable apparatuses for condensation are in particular spray scrubbers, Venturi scrubbers, bubble columns or apparatuses having sprayed surfaces.

The mixture obtained by partial or total condensation of the reaction product from stage (a), in particular the condensate of the medium boiler fraction in the case of condensation in a column, preferably contains from 60 to 99.5% by weight of acrylic acid, from 0.1 to 40% by weight of water and in addition from 0.1 to 15% by weight of impurities, in particular, based in each case on 100% by weight of condensate, from 0.01 to 5% by weight of acrolein, from 0.05 to 5% by weight of acetic acid, from 0.01 to 5% by weight of propionic acid, from 0.01 to 5% by weight of formaldehyde, from 0.01 to 5% by weight of further aldehydes and from 0.01 to 5% by weight of maleic acid. Particularly preferably, a mixture which contains from 85 to 98% by weight of acrylic acid, from 0.5 to 14% by weight of water and in addition from 0.5 to 5% by weight of impurities, in particular, based in each case on 100% by weight of condensate, from 0.01 to 3% by weight of acrolein, from 0.1 to 3% by weight of acetic acid, from 0.01 to 3% by weight of propionic acid, from 0.01 to 3% by weight of formaldehyde, from 0.01 to 3% by weight of further aldehydes and from 0.01 to 3% by weight of maleic acid, is obtained in the condensation.

Stage (c)

60 In stage (c), the solution obtained in stage (b) and having a higher acrylic acid concentration is crystallized. Thus, the solution obtained in the condensation stage is fed directly to the crystallization. The crystallization can be carried out continuously or batchwise, in one stage or a plurality of stages. Preferably, the crystallization is effected in one stage. All crystallization methods in which the crystallized solution/melt is thoroughly mixed by stirring or circulation

are suitable, both continuous and batchwise procedures. Preferably used apparatuses are stirred kettle crystallizers and forced circulation crystallizers but draught-tube and fluidized-bed crystallizers may also be used.

According to the invention, the solution is partly evaporated in the crystallization. The crystallizing solution features the boiling point which is dependent on the pressure in the crystallization. The pressure in the crystallization is brought to the desired value by means of an apparatus for generating reduced pressure. Said apparatus is not subject to any restriction here. All systems which reach the desired reduced pressure in one stage or a plurality of stages by mechanical and/or thermal compression are suitable. Liquid ring pumps, in particular in combination with vapor-jet pumps, vapor-jet pumps alone or Roots pumps or rotary vane pumps are preferably used. The pressures to be established are dependent on the composition of the crystallizing solution. They are expediently from 1 to 15, preferably from 3 to 8, mbar (absolute).

Advantageously, the temperature of the solution during crystallization is from -10 to +14°C, in particular from -5 to +10°C. The crystallization is advantageously operated so that a solids content of from 5 to 60 g of solid per 100 g of suspension is established, contents of from 15 to 45 g of solid per 100 g of suspension being preferred.

Stage (d)

In stage (d), the acrylic acid crystals obtained in stage (c) are separated from the mother liquor. All known solid-liquid separation methods are suitable for this purpose. In a preferred embodiment of the invention, the crystals are separated from the mother liquor by filtration and/or centrifuging. Advantageously, the filtration or centrifuging is preceded by preliminary thickening of the suspension, for example by hydrocyclone(s). All known centrifuges which operate batchwise or continuously are suitable for the centrifuging. Reciprocating centrifuges which can be operated in one stage or a plurality of stages are most advantageous. Helical-screen centrifuges or helical-conveyor centrifuges (decanters) are also suitable. Filtration is advantageously effected by means of suction filters, which are operated batchwise or continuously, with or without a stirrer, or by means of belt filters. In general, the filtration can be carried out under superatmospheric or reduced pressure.

Further process steps for increasing the purity of the crystals or the crystal cake can be provided during and/or after the solid-liquid separation. In a particularly advantageous embodiment of the invention, the separation of the crystals from the mother liquor is followed by one-stage or multistage washing and/or sweating of the crystals or of the crystal cake. During the washing, the amount of wash liquid is suitably from 0 to 500, preferably from 30 to 200, g of wash liquid/100 g of crystals. The wash liquid used is not subject to any restriction. However, washing is advantageously carried out using pure product, i.e. using a liquid which contains acrylic acid whose purity is higher than that of the crystal cake to be washed, but at least purer than the mother liquor in the crystallization. Washing with water is also possible. The washing can be effected in apparatuses suitable for this purpose. Wash columns in which the separation of the mother liquor and the washing are effected in one apparatus, centrifuges which can be operated in one stage or a plurality of stages or suction filters or belt filters are advantageously used. The washing can be carried out on centrifuges or belt filters in one stage or a plurality of stages. Here, the wash liquid can be fed countercurrent to the crystal cake.

Sweating comprises local melting of contaminated regions. Advantageously, from 0 to 100 g of crystals are melted during the sweating per 100 g of crystals before the sweating, preferably from 5 to 35 g of crystals are melted per

5 100 g of crystals. The sweating is particularly preferably carried out on centrifuges or belt filters. It may also be suitable to carry out a combination of washing and sweating in one apparatus.

The acrylic acid crystals after the solid-liquid separation 10 and any further washing and/or sweating constitute the purified acid from the process. The purity of the crystals obtained is as a rule from 97 to 99.9, in particular from 98.5 to 99.9, % by weight of acrylic acid. The crystals prepared by the novel process now contain only very small amounts of impurities, such as acetic acid, maleic acid or aldehydes.

If desired, the purified acid can be esterified by known methods or further purified by known methods.

Stage (e)

20 In stage (e), the mother liquor from stage (d), which remains behind after isolation of the crystals, is at least partly recycled directly to the condensation stage (b). The amount of recycled mother liquor is from 0 to 100, in particular from 80 to 100, preferably 100, % by weight. If the condensation is carried out in a column, the mother liquor is expediently recycled to below the side take-off of the column, preferably in the region between the first cooling loop and the side take-off, most preferably in the region just below or a few trays below the side take-off of the column.

Stage (f)

30 In stage (f), at least a part of the solution evaporated in stage (c) is recycled to the condensation stage (b). The amount of solution recycled to stage (b) is from 0 to 100, in particular from 50 to 100, preferably from 80 to 100, most preferably about 100, % by weight. If the condensation is carried out in a column, the evaporated solution is expediently recycled to above the side take-off of the column, preferably in the region between the side take-off and the second cooling loop, most preferably in the region just above or a few trays above the side take-off of the column. That part of the evaporated solution which is not recycled to stage (b) is advantageously recycled to the crystallization stage (c). It is also possible to remove evaporated solution, expediently not more than 80% by weight of the evaporated solution being removed.

40 The recycling of the evaporated solution to (b) and, if 50 required, stage (c) is not subject to any restriction at all with regard to the phase state (gaseous, partly condensed, completely condensed). The recycling is preferably effected in the liquid state after carrying out a partial or total condensation of the evaporated solution. Here, the condensation methods and apparatuses and the production of the mass-transfer and heat-exchange surfaces required for the condensation are not subject to any restriction at all. The exchange surface(s) may be in the form of conventional surface condensers, such as tube-bundle condensers or plate-type heat exchangers. The exchange surfaces are however preferably formed by spraying liquids, for example already obtained condensate and/or by trickling appropriate liquid or causing it to flow over apparatus surfaces and/or baffles and/or packings. Here, it is possible to mix a liquid removed 60 from a suitable point in the process with the condensate and to use this mixture for producing the exchange surface. The liquid to be mixed with the condensate is expediently chosen

so that the resulting mixture has a lower freezing point than the condensate itself. Depending on the composition of the vapor removed in the crystallization (c), suitable points for withdrawing mixing liquid when carrying out the condensation stage (b) in a column may be side take-offs of the column or liquid/suspension side take-offs from stage (c) and (d). Acrylic acid purified by crystallization or water supplied from outside are also possible as mixing liquid. Preferably at least 90%, in particular at least 95%, of the evaporated solution are condensed. Most preferably, the total condensable amount of the evaporated solution is condensed. Uncondensable fractions of the evaporated solution are expediently removed via the apparatus for reduced pressure generation in stage (c). In addition to the partial or total condensation of the evaporated solution, it is also possible to recycle the evaporated solution in gaseous form to stage (b), which however is more expensive owing to the compressors or pumps required.

It is also possible to introduce components or mixtures which have a lower boiling point than that of acrylic acid at a suitable point into the crystallization (c) or into stages connected with it, in order that the reduced pressure required for a desired crystallization temperature does not have to be so low. Suitable points here are the crystallization stage (c) itself and its feed stream arriving from stage (b) and the stage (f) in the case of partial recycling of the evaporated solution to stage (c). In addition to the partial or total condensation of the evaporated solution, it is also possible to recycle the evaporated solution in gaseous form to stage (b), which however is more expensive owing to the compressors or pumps required.

The figure shows a preferred embodiment for carrying out the novel process. Air is fed to the synthesis reactors 4 and 5 via line 2 and compressor 3. In addition, recycle gas compressed by compressor 6 and essentially consisting of nitrogen, carbon oxides and unconverted starting materials, and propene originating from line 1, are fed to the reactor 4 via line 9. The first stage of the two-stage gas-phase oxidation, i.e. the oxidation of propene to acrolein, takes place in synthesis reactor 4. In synthesis reactor 5, the acrolein is then oxidized to the corresponding acid. A gaseous product mixture which, in addition to the acid, contains further, above-mentioned impurities is formed here. Said product mixture is fed via line 7 to the condenser 8, in which it is cooled and condensed. The condenser 8 is in the form of a column in the figure. The uncondensed part of the product mixture is removed via line 9, a part thereof being recycled as recycle gas, as described above, to reactor 4 and the other part, preferably 50% of the total stream of line 9, being removed as waste gas from the plant via line 10. The condensed high boiler fraction is removed via line 18 while the condensed low boiler fraction is removed via line 19. The condensed medium boiler fraction, which contains the major part of the acrylic acid, is fed via line 11 (side take-off) to the crystallization apparatus 12 in which the crystallization is carried out. The mother liquor from the crystallization is fed together with the crystals via line 13 to a suitable apparatus 14 for solid-liquid separation, the crystals being removed via line 15 and the mother liquor via line 16. At least a part of the mother liquor is fed via line 17 into the condenser 8, preferably below the side take-off (line 11) and thus fed back to the condensation. The purified acid is thus removed via line 15. In the crystallization apparatus 12, a part of the solution is evaporated under reduced pressure which is generated by the apparatus 25 for generating

reduced pressure, and said part is fed via line 21 to the condensation apparatus 20. In this, the evaporated solution is virtually completely converted into the condensed phase. The condensed phase is partly recycled via line 22 to the crystallization apparatus 12 and partly fed via line 23 to the condensation apparatus 8, preferably above the side take-off (line 11). Those fractions of the evaporated solution which are not condensed in the apparatus 20 are fed via line 24 to the apparatus 25 and are removed therefrom, and from the process, via line 26 as waste gas.

By recycling mother liquor and, preferably condensed, vapors to the condensation stage, the present invention permits high yield. The heat evolved in the crystallization stage is removed from the crystallization in a simple manner by evaporating some of the solution. At the same time, a part of the work required for separating acrylic acid and low boilers (in comparison with acrylic acid) is performed by evaporating some of the solution in the crystallization.

Compared with the processes known to date, the novel process has the further advantage that, after condensation of the product mixture formed in the gas-phase oxidation, an acid of very good quality is obtained by crystallization directly from the solution formed in the condensation. With the use of a crystallization comprising more than one purification stage, pure acid can be produced directly, no preliminary purification being necessary, in contrast to the abovementioned publications, Canadian Patent 790 625, JP-A-0 07 082 210-A and EP-A-0 616 998.

A further important advantage of the novel process is that the process is carried out at relatively low temperatures, i.e. the main stream of acrylic acid is removed from the process as product directly via condensation and crystallization. Since, in contrast to the prior art, no assistant is added and hence no high thermal load (in particular in the case of high acrylic acid contents) is required for separating off the assistant, polymerization problems and the use of process stabilizers, as encountered here in the prior art, are reduced. Moreover, this also avoids or reduces fouling. It is surprising that -acrylic acid solutions obtained by gas-phase oxidation and condensation can be directly crystallized and that products of very high purity are obtained thereby. In particular, it was surprising that this is also possible in the case of aqueous condensates.

The following example, which represents a preferred embodiment of the invention, illustrates the invention.

Example

The following mixture at a temperature of 270° C. was obtained from reaction stage (a) by catalytic gas-phase oxidation of propene.

TABLE 1

| Component | Concentration in % by weight |
|--------------------|------------------------------|
| Water | 4.4 |
| Formaldehyde | 0.2 |
| Acetic acid | 0.4 |
| Acrylic acid | 10.1 |
| Maleic anhydride | 0.07 |
| Benzoic acid | 0.02 |
| Acrolein | 0.1 |
| Phthalic anhydride | 0.01 |
| Propionic acid | 0.002 |
| Maleic acid | 0 |
| Allyl acrylate | 0.001 |
| Benzaldehyde | 0.0005 |
| Furfural | 0.0015 |
| Phenothiazine | 0 |
| Nitrogen | 76.5 |

TABLE 1-continued

| Component | Concentration in % by weight |
|-----------------|------------------------------|
| Oxygen | 3.6 |
| Carbon monoxide | 0.7 |
| Carbon dioxide | 2.6 |
| Propene | 0.5 |
| Propane | 0.7 |

The mixture (10867 g/h) was fed to the condensation stage (b). The condensation apparatus used was a tray column having 27 bubbles trays. The temperature in the bottom of the column was 100° C. The heat of condensation was removed via heat exchangers at trays 1 and 27. Above the side take-off of the column, phenothiazine was added as a stabilizer. At tray 27, a stream of 269 g/h having the following composition was taken off:

TABLE 2

| Component | Concentration in % by weight |
|--------------------|------------------------------|
| Water | 89.3 |
| Formaldehyde | 0.075 |
| Acetic acid | 9.5 |
| Acrylic acid | 1.1 |
| Maleic anhydride | 0 |
| Benzoic acid | 0 |
| Acrolein | 0.028 |
| Phthalic anhydride | <0.0001 |
| Propionic acid | <0.0001 |
| Maleic acid | <0.0001 |
| Allyl acrylate | <0.0001 |
| Benzaldehyde | <0.0001 |
| Furfural | <0.0001 |
| Phenothiazine | <0.0001 |
| Nitrogen | 0 |
| Oxygen | 0 |
| Carbon monoxide | 0 |
| Carbon dioxide | 0 |
| Propene | 0 |
| Propane | 0 |

At the bottom of the column, a stream of 17.8 g/h having the following composition was taken off:

TABLE 3

| Component | Concentration in % by weight |
|--------------------|------------------------------|
| Water | 1.3 |
| Formaldehyde | 0.0033 |
| Acetic acid | 0.9 |
| Acrylic acid | 33.1 |
| Maleic anhydride | 40.3 |
| Benzoic acid | 12.2 |
| Acrolein | 0.01 |
| Phthalic anhydride | 6.1 |
| Propionic acid | 0.045 |
| Maleic acid | <0.0001 |
| Allyl acrylate | 0.02 |
| Benzaldehyde | 0.3 |
| Furfural | 0.5 |
| Phenothiazine | 5.2 |
| Nitrogen | 0 |
| Oxygen | 0 |
| Carbon monoxide | 0 |
| Carbon dioxide | 0 |
| Propene | 0 |
| Propane | 0 |

At tray 11, a liquid stream of 4955 g/h at 95° C. was taken off from the column and was then crystallized. This stream had the following composition:

TABLE 4

| Component | Concentration in % by weight |
|--------------------|------------------------------|
| Water | 1.5 |
| Formaldehyde | 0.005 |
| Acetic acid | 6 |
| Acrylic acid | 91.5 |
| Maleic anhydride | 0.6 |
| Benzoic acid | <0.0001 |
| Acrolein | 0.011 |
| Phthalic anhydride | <0.0001 |
| Propionic acid | 0.069 |
| Maleic acid | <0.0001 |
| Allyl acrylate | 0.2 |
| Benzaldehyde | 0.001 |
| Furfural | 0.1 |
| Phenothiazine | 0.016 |
| Nitrogen | 0 |
| Oxygen | 0 |
| Carbon monoxide | 0 |
| Carbon dioxide | 0 |
| Propene | 0 |
| Propane | 0 |

The mixture originating from tray 11 was then crystallized in a 10 l stirred container with a helical ribbon agitator. The heat of crystallization was removed by partial evaporation. The crystallization temperature of the solution was 6.5° C. The pressure was 3 mbar. The suspension produced during the crystallization was separated into crystals and mother liquor on a centrifuge at 2000 rpm (centrifuge diameter 250 mm) and in a centrifuging time of 1 minute. The crystals (1486 g/h) were then washed with melted crystals (323 g/h) for 1 min at 2000 rpm.

The mother liquor was recycled together with the wash liquid to tray 10 of the condensation column (3060 g/h). The solution evaporated in the crystallization was recycled to tray 15 of the column after condensation (732 g/h). The composition of this stream was:

TABLE 5

| Component | Concentration in % by weight |
|--------------------|------------------------------|
| Water | 6.7 |
| Formaldehyde | 0.034 |
| Acetic acid | 14.2 |
| Acrylic acid | 78.1 |
| Maleic anhydride | 0.1 |
| Benzoic acid | <0.0001 |
| Acrolein | 0.072 |
| Phthalic anhydride | <0.0001 |
| Propionic acid | 0.069 |
| Maleic acid | <0.0001 |
| Allyl acrylate | 0.4 |
| Benzaldehyde | <0.0001 |
| Furfural | 0.069 |
| Phenothiazine | 0 |
| Nitrogen | 0 |
| Oxygen | 0 |
| Carbon monoxide | 0 |
| Carbon dioxide | 0 |
| Propene | 0 |
| Propane | 0 |

Analysis of the crystals gave the following composition:

TABLE 6

| Component | Concentration in % by weight |
|--------------|------------------------------|
| Water | 0.026 |
| Formaldehyde | 0 |

TABLE 6-continued

| Component | Concentration in % by weight |
|--------------------|------------------------------|
| Acetic acid | 0.8 |
| Acrylic acid | 99.1 |
| Maleic anhydride | 0.04 |
| Benzoic acid | 0 |
| Acrolein | 0 |
| Phthalic anhydride | 0 |
| Propionic acid | 0.02 |
| Maleic acid | 0 |
| Allyl acrylate | 0.01 |
| Benzaldehyde | <0.0001 |
| Furfural | 0.007 |
| Phenothiazine | 0.003 |
| Nitrogen | 0 |
| Oxygen | 0 |
| Carbon monoxide | 0 |
| Carbon dioxide | 0 |
| Propene | 0 |
| Propane | 0 |

As shown in Table 6, the novel process permits the preparation of pure acrylic acid.

We claim:

1. A process for the preparation of acrylic acid by:
 - (a) preparation of a gaseous product mixture which essentially has the composition of a reaction mixture of catalytic gas-phase oxidation of C₃-alkanes, C₃-alkenes, C₃-alkanols and/or C₃-alkanals and/or precursors thereof to acrylic acid, which comprises
 - (b) condensation of the gaseous product mixture,
 - (c) crystallization of the acrylic acid from the solution obtained in stage (b), with partial evaporation of the solution under reduced pressure,
 - (d) isolation of the resulting crystals from the mother liquor,
 - (e) recycling of at least a part of the mother liquor from stage (d) to stage (b) and
 - (f) recycling of at least a part of the evaporated solution from stage (c) to stage (b).
2. A process as claimed in claim 1, wherein the crystals in stage (d) are separated from the mother liquor by filtration and/or centrifuging.
3. A process as claimed in claim 1, wherein the crystals isolated in stage (d) are subjected to at least one washing and/or sweating procedure.
4. A process as claimed in claim 1, wherein, in stage (e) from 80 to 100% by weight of the mother liquor from stage (d) are recycled to stage (b).
5. A process as claimed in claim 1, wherein, in stage (f), from 50 to 100% by weight of the evaporated solution from stage (c) are recycled to stage (b).
6. A process as claimed in claim 5, wherein that part of the evaporated solution which is not recycled to stage (b) is recycled to stage (c).
7. A process as claimed in claim 1, wherein at least 90% by weight of the evaporated solution from stage (c) are condensed before recycling to stage (b) and, if required, stage (c).
8. A process for the preparation of acrylic acid by:
 - (a) preparation of a gaseous product mixture which essentially has the composition of a reaction mixture of catalytic gas-phase oxidation of C₃-alkanes, C₃-alkenes, C₃-alkanols and/or C₃-alkanals and/or intermediates thereof to acrylic acid, which comprises
 - (b) condensation of the gaseous product mixture,
 - (c) crystallization of the acrylic acid from the solution obtained in stage (b), with partial evaporation of the solution under reduced pressure,
 - (d) isolation of the resulting crystals from the mother liquor,
 - (e) recycling 80 to 100% by weight of the mother liquor from stage (d) to stage (b) and
 - (f) recycling 50 to 100% by weight of the evaporated solution from stage (c) to stage (b).
17. A process for the preparation of acrylic acid by:
 - (a) preparation of a gaseous product mixture which essentially has the composition of a reaction mixture of catalytic gas-phase oxidation of C₃-alkanes, C₃-alkenes, C₃-alkanols and/or C₃-alkanals and/or intermediates thereof to acrylic acid, which comprises
 - (b) condensation of the gaseous product mixture,
 - (c) crystallization of the acrylic acid from the solution obtained in stage (b), with partial evaporation of the solution under reduced pressure,
 - (d) isolation of the resulting crystals from the mother liquor,
 - (e) recycling 80 to 100% by weight of the mother liquor from stage (d) to stage (b) and
 - (f) recycling 50 to 100% by weight of the evaporated solution from stage (c) to stage (b).
18. A process as claimed in claim 17, wherein that part of the evaporated solution which is not recycled to stage (b) is recycled to stage (c).
19. A process as claimed in claim 17, wherein at least 90% by weight of the evaporated solution from stage (c) are condensed before recycling to stage (b) and, if required, stage (c).
20. A process as claimed in claim 1, wherein the crystallization in stage (c) is carried out at from 1 to 15 mbar (absolute) and at from -10 to +14° C.

(b) condensation of the gaseous product mixture,

(c) crystallization of the acrylic acid from the solution obtained in stag (b) with partial evaporation of the solution under reduced pressure,

(d) isolation of the resulting crystals from the mother liquor,

(e) recycling of at least a part of the mother liquor from stage (d) to stage (b) and

10 (f) recycling of at least a part of the evaporated solution from stage (c) to stage (b), wherein the condensation in stage (b) is carried out in a column having baffles which effect separation.

9. A process as claimed in claim 11, wherein, in the condensation, the solution to be crystallized in stage (c) is removed as the medium boiler fraction from the column.

10. A process as claim 8, wherein the crystallization in stage (c) is carried out at from 1 to 15 mbar (absolute) and at from -10 to +14° C.

11. A process as claimed in claim 8, wherein the crystals in stage (d) are separated from the mother liquor by filtration and/or centrifuging.

12. A process as claimed in claim 8, wherein the crystals isolated in stage (d) are subjected to at least one washing and/or sweating procedure.

13. A process as claimed in claim 8, wherein, in stage (e), from 80 to 100% by weight of the mother liquor from stage (d) are recycled to stage (b).

14. A process as claimed in claim 8, wherein, in stage (f), from 50 to 100% by weight of the evaporated solution from stage (c) are recycled to stage (b).

15. A process as claimed in claim 14, wherein that part of the evaporated solution which is not recycled to stage (b) is recycled to stage (c).

16. A process as claimed in claim 8, wherein at least 90% by weight of the evaporated solution from stage (c) are condensed before recycling to stage (b) and, if required, stage (c).

17. A process for the preparation of acrylic acid by:

- (a) preparation of a gaseous product mixture which essentially has the composition of a reaction mixture of catalytic gas-phase oxidation of C₃-alkanes, C₃-alkenes, C₃-alkanols and/or C₃-alkanals and/or intermediates thereof to acrylic acid, which comprises
 - (b) condensation of the gaseous product mixture,
 - (c) crystallization of the acrylic acid from the solution obtained in stage (b), with partial evaporation of the solution under reduced pressure,
 - (d) isolation of the resulting crystals from the mother liquor,
 - (e) recycling 80 to 100% by weight of the mother liquor from stage (d) to stage (b) and
 - (f) recycling 50 to 100% by weight of the evaporated solution from stage (c) to stage (b).

18. A process as claimed in claim 17, wherein that part of the evaporated solution which is not recycled to stage (b) is recycled to stage (c).

19. A process as claimed in claim 17, wherein at least 90% by weight of the evaporated solution from stage (c) are condensed before recycling to stage (b) and, if required, stage (c).

20. A process as claimed in claim 1, wherein the crystallization in stage (c) is carried out at from 1 to 15 mbar (absolute) and at from -10 to +14° C.

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United States Patent [19]

Ember

US005245093A
[11] Patent Number: 5,245,093
[45] Date of Patent: Sep. 14, 1993

[54] **REACTION PROCESSES IN A
MULTI-STAGE FLUIDIZED BED**

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[21] Appl. No.: 301,876

[22] Filed: Jan. 26, 1989

[51] Int. Cl. 5 C07C 5/10; C08G 85/00;
B01J 8/18; B01J 2/34

[52] U.S. Cl. 585/266; 422/127;
422/134; 422/142; 422/147; 502/41; 502/43;
526/65; 549/249; 549/258; 549/262; 549/523;
562/545; 564/305; 568/449; 568/716; 568/895;
568/910

[58] Field of Search 208/108, 164, 156, 158;
502/43, 48, 56; 34/164; 422/127, 145, 142;
526/65; 585/265, 266

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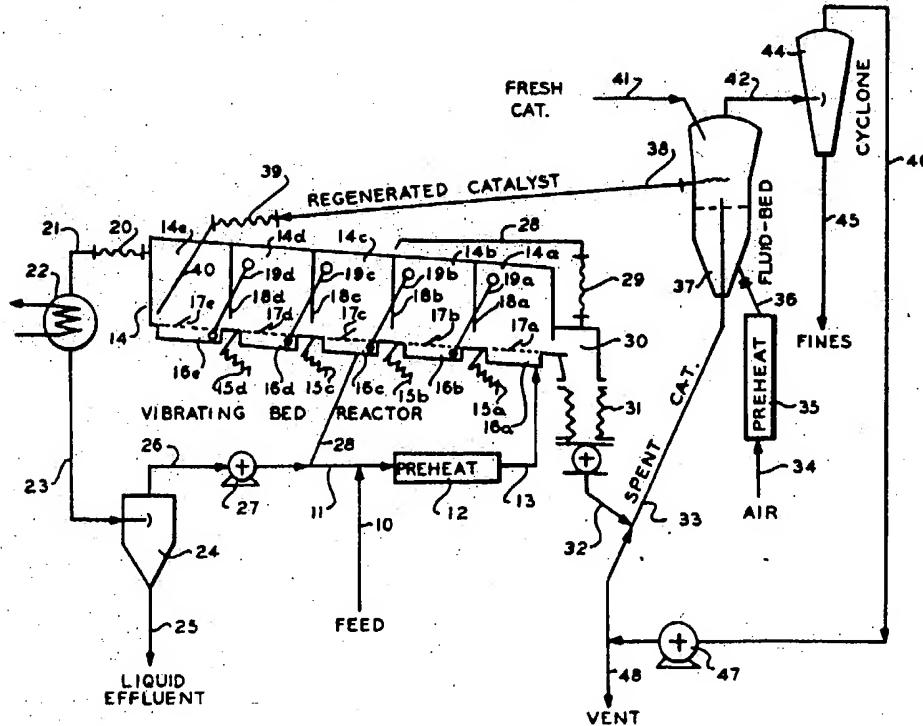
Primary Examiner—Paul E. Konopka

Attorney, Agent, or Firm—Elliot M. Olstein; Raymond J. Lillie

[57] ABSTRACT

A process for reacting a fluid phase (gaseous and/or liquid phase) in contact with a solid phase in a reaction zone, wherein the improvement in said process comprises reacting the fluid phase in contact with the solid phase in a horizontally-oriented fluidized bed vessel. The vessel includes at least two compartments or stages, and includes means for vibrating the vessel. The process of the present invention enables one to effect fluidization of the solid phase independently of the flow rate or velocity of the fluid phase, thus enabling proper contact time of the fluid phase with the solid phase and minimizing the amount of fluid phase reactant to be recycled.

5 Claims, 3 Drawing Sheets



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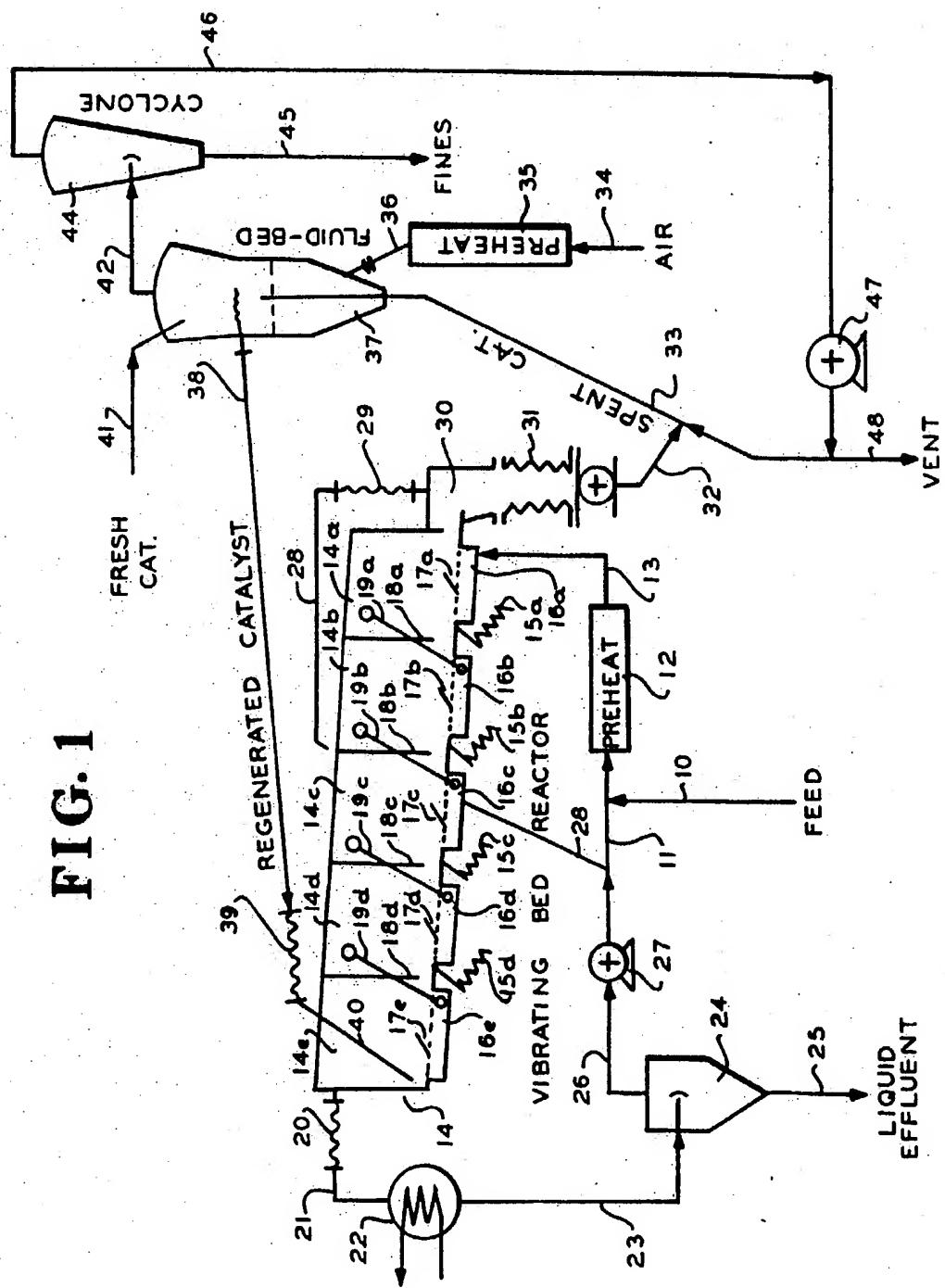


FIG. 2

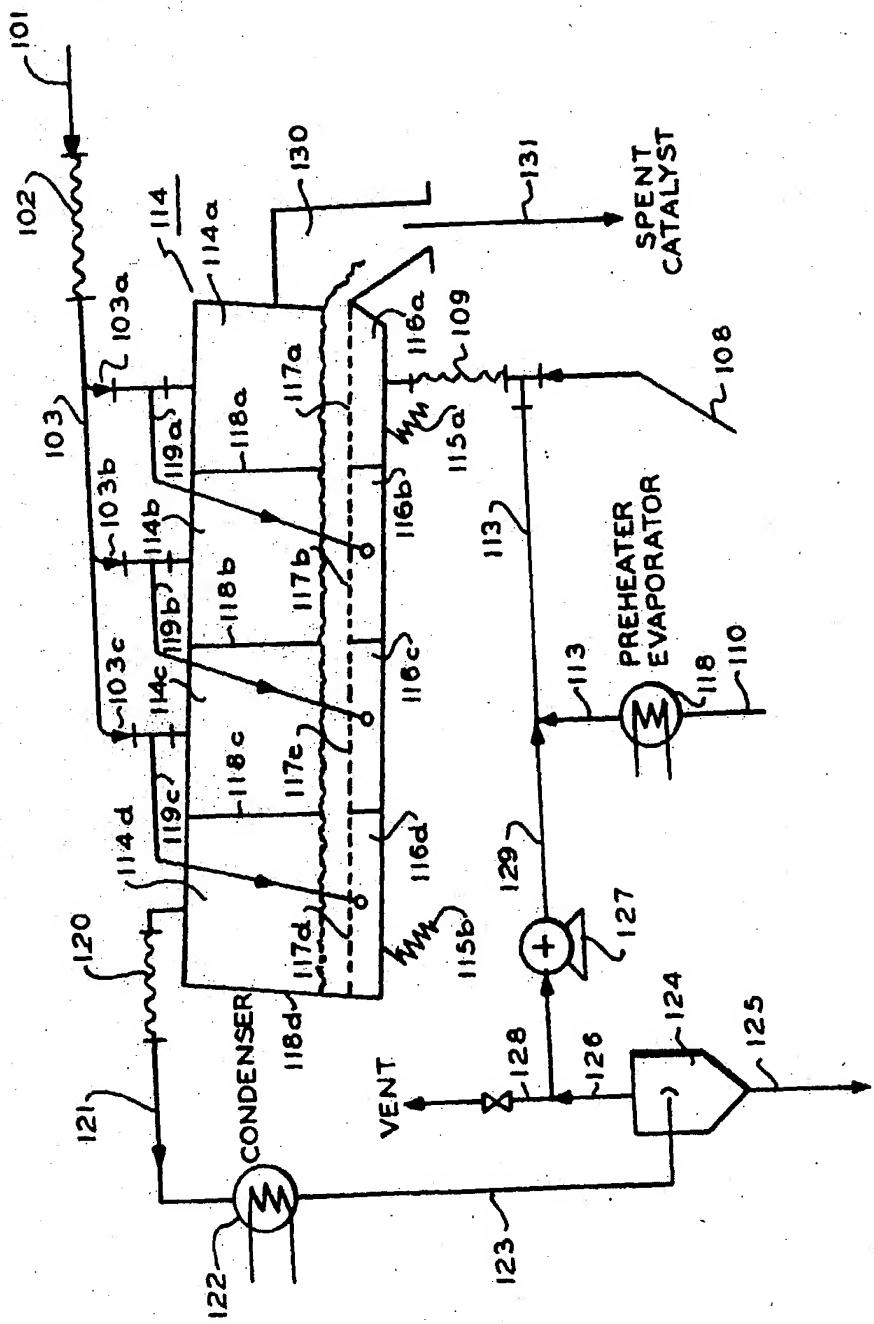
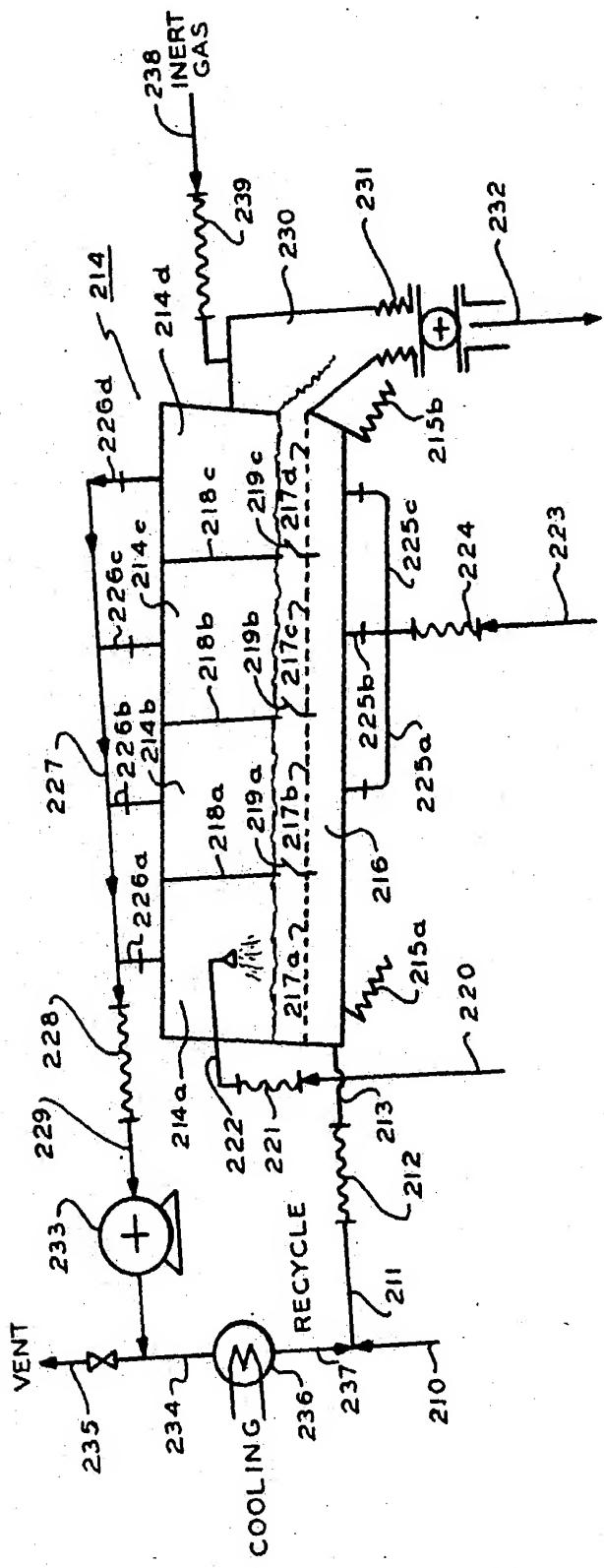


FIG. 3



REACTION PROCESSES IN A MULTI-STAGE
FLUIDIZED BED

This invention relates to a fluidized bed vessel, and the use thereof for contacting a fluid phase with a solid phase in said vessel.

This invention further relates to a new and improved process for effecting a reaction in a fluidized bed vessel.

More particularly, this invention relates to effecting a reaction in a fluidized bed vessel by providing a multi-stage vibrating fluidized bed, whereby the fluidization of the solid phase is independent of the flow of the fluid phase through the vessel.

Reactions in which a fluid phase, a gaseous (vapor) or liquid phase, is contacted with a solid phase, said solid phase being a solid reactant or a catalyst, are usually carried out either in fixed bed or fluidized bed reactors. The use of a fixed bed reactor, however, requires periodic shutdowns of the reactor in order to regenerate or reactivate the catalyst, or duplication of the reactor, both of which result in increased costs. Moving bed reactors, designed to solve the problem of shutting down the reactor in order to regenerate the catalyst, presented a costly solids handling problem connected with the continuous removal of inactive catalyst from the reactor.

The use of a fluidized bed reactor of the circulating catalyst type integrates truly continuous fluidized bed reaction and catalyst regeneration steps. In addition, high heat and mass transfer rates eliminate so-called "hot spots" (by minimizing the temperature gradients) in the fluid bed reactor. The close control of the reaction temperature improves the selectivity of highly exothermic reactions having an unstable product or intermediate.

The fluidized bed reactor, however, requires a high velocity of a fluid phase (e.g., gaseous and/or vapor phase) reactant in order to fluidize the solids (e.g., catalyst) in the bed. The high velocity of the fluid phase limits the residence time of the fluid phase reactant in the catalyst bed. The short residence time of the fluid phase reactant lessens the chances of reaction of the fluid phase reactant in its entirety and increases the need for the recycle of the reactant or reactants.

In accordance with an aspect of the present invention, there is provided an improvement in a process for reacting a fluid phase in contact with a solid phase in a reaction zone. The improvement comprises reacting the fluid phase in contact with the solid phase in a horizontally oriented fluidized bed vessel. The fluidized bed vessel includes at least two compartments defined by partition means allowing for solids flow between said at least two compartments. The fluidized bed vessel includes means for vibrating the fluidized bed vessel. The solids of the solid phase are passed from one compartment to another during said reaction of the fluid phase in contact with the solid phase. The fluid phase may move countercurrently to the direction of movement of the solids, or the fluid phase may move cocurrently with the direction of movement of the solids or the fluid phase in each compartment may not flow to another compartment; i.e., separate fluid inlets and outlets for each compartment. When the reactor has separate fluid inlets and outlets for each compartment, there may be provided cross-current movement of the fluid phase in relation to the direction of movement of solids. In each compartment, the flow of the fluid phase may be

through the solid phase; i.e., the fluid phase moves transverse to the movement of the solid phase. In cases where the fluid phase flows from one compartment to another, the flow of the fluid phase may be cocurrent or countercurrent to the direction of movement of the solid phase.

The fluid phase may be in a vapor phase and/or a liquid phase. The solid phase may be comprised of a catalyst. The catalyst may be selected from the class comprising aluminosilicate catalysts, such as zeolite catalysts, phosphoric acid, and molybdate-vanadium catalysts.

In one embodiment, each of the at least two compartments includes an inlet means and an outlet means, and wherein the fluid phase is introduced into at least two of said inlet means, and effluent is withdrawn and recovered from at least two of said outlet means.

The process may further comprise withdrawing at least a portion of the solids from the vessel after passage of the solids through the at least two compartments, regenerating the solids in a regeneration zone, and recycling the solids to the vessel for passage through the at least two compartments. The regeneration zone may comprise a fluidized bed reactor, wherein fluidization of the solids and regeneration of the solids is accomplished by passage of a heated gas through the fluidized bed reactor.

In a preferred embodiment, at least the solid phase moves in substantially plug flow. The fluid phase may also move in plug flow and plug flow of the fluid phase through the vessel may be cocurrent or countercurrent to the movement of the solid phase.

In accordance with another aspect of the present invention, a fluid phase reactant or reactants in the form of a vapor is polymerized in the presence of a solid phase catalyst in the fluidized bed vessel. Examples of such polymerizations include the formation of polyethylene from ethylene, the formation of polypropylene from propylene, and the copolymerization of polyethylene with polypropylene or polybutylene. As the polymerization or copolymerization reaction progresses (i.e., increase in length and molecular weight of polymer chain), a solid phase polymer is formed, which is deposited with the solid catalyst in the fluidized beds of the vessel, and the solid polymer moves from compartment to compartment with the catalyst. Because in such polymerizations only a small amount of catalyst is required one can withdraw the polymer from the vessel along with the catalyst, and catalyst regeneration is not necessary. Such polymerization reactions may be carried out at a temperature of from about 60° C. to about 100° C., preferably from about 70° C. to about 80° C., and at a pressure of about 300 psig.

The fluidized bed vessel, in another aspect of the present invention, may be used for fluid phase reactions in the presence of a catalyst wherein a vapor phase and/or liquid phase reactant is reacted in the presence of a solid catalyst to form a vapor phase and/or liquid phase product.

Such reactions include those that are exothermic, such as hydrogenations, oxidation reactions, chlorinations, ammonolyses and ammonoxidation, oxidation, and vapor phase nitrations; for example, the production of maleic anhydride from n-butane, 1, 3-butadiene, or C₄ to C₁₀ hydrocarbons.

Specific examples of these reactions include the production of ethylene oxide, from ethylene, and propylene oxide from propylene, either of which may take place at

about 250° C. and at about 15 psig. Isobutane may be oxidized to produce tertbutyl alcohol, or isobutylene may be oxidized to produce methacrylic acid, at a temperature of about 300° C. and a pressure of about 20 psig. O-xylene may be converted to phthalic anhydride, 5 at a temperature of about 380° C. to about 420° C., and at a pressure of about 15 psig. Ethylene may be reacted to form acetaldehyde at a temperature of about 140° C. and a pressure of about 15 psig. Acrolein and/or acrylonitrile may be produced from propylene at a 10 temperature of about 450° C. and a pressure of about 15 psig. Nitrobenzene may be reacted to form aniline at a temperature of from about 250° C. to about 350° C., and at a pressure of about 15 psig.

Other reactions include the alkylation of phenols 15 with methanol to produce cresols, xlenols, or trimethyl phenols. These reactions may be carried out at about 360° C., and a pressure of about 30 psig. Ethylene and H₂O may be reacted to form ethanol at a temperature of from about 200° C. to about 300° C., and a pressure of about 15 psig, whereas tert-butyl alcohol may be dehydrated to produce isobutylene at a temperature of from about 200° C. to about 300° C., and a pressure of about 15 psig. Hydrogenation reactions include the hydrogenation of benzene to form cyclohexane at a 25 temperature of from about 150° C. to about 250° C., and at a pressure of about 300 psig. In addition, aromatic nitriles may be produced from alkyl aromatics such as phthalonitrile from xylenes, nicotinonitriles from alkyl pyridines, etc.

The invention will now be described with respect to the drawings, wherein:

FIG. 1 is a schematic of a first embodiment within the scope of the present invention wherein a multi-stage vibrating fluidized bed reactor is employed in a reaction 35 of a fluid phase reactant in the presence of a solid phase catalyst to produce a fluid phase product:

FIG. 2 is a schematic of a second embodiment within the scope of the present invention depicting an oxidation reaction wherein oxygen is added through inlet 40 means to each stage of the multi-stage vibrating fluidized bed: and

FIG. 3 is a schematic of a third embodiment within the scope of the present invention wherein a multi-stage vibrating fluidized bed reactor is employed in a copolymerization of fluid phase monomers to produce a solid 45 phase polymer product.

Referring now to the drawings as shown in FIG. 1, a feedstock in line 10 is passed to line 11, and then heated in preheater 12. In the embodiment shown in FIG. 1, 50 the feedstock is one to be employed in an exothermic reaction as described above, wherein a fluid phase reactant, preferably a vapor phase reactant, is reacted in the presence of a solid catalyst to form a fluid phase, preferably a vapor phase, product. Examples of such reactions 55 are hereinabove described. The feed which is preheated in preheater 12 comprises one or more reactants. The preheater is operated at temperature and pressure conditions well known in the art, said conditions depending upon the feed employed. After being heated, the feed is withdrawn from preheater 12 through line 13 and passed to distributor 16a of stage 14a of horizontally 60 oriented vibrating fluidized bed reactor 14.

Vibrating bed reactor 14 is comprised of compartments or stages 14a, 14b, 14c, 14d, and 14e. At the bottom of each of stages 14a through 14e of reactor 14 are mixing zones 16a through 16e, wherein the fluid phase or vapor phase reactants, and any reaction product

from a previous stage is introduced prior to passing the vapor phase through a catalyst bed. Above each of mixing zones 16a through 16e lies screens 17a through 17e, upon each of which lies a bed of catalyst. The catalyst is passed in plug flow through stages 14a to 14e, and the catalyst beds in each stage of the reactor 14 are fluidized upon vibration of the reactor 14. Reactor 14 may also be inclined from stage 14a to 14e to aid in the passing of the solid catalyst between stages. The reactor is connected to a vibrating means (not shown), which moves springs 15a, 15b, 15c, and 15d, thereby causing vibration of the reactor. Although five stages, 14a through 14e of reactor 14 are shown, it is contemplated that the number of stages or compartments may vary, as long as at least two stages or compartments are present.

Contained within reactor 14 are partitioning means 18a, 18b, 18c, and 18d, which separate the reactor into compartments 14a through 14e.

The vapor phase reactant, which is fed to mixing zone 16a of stage 14a of reactor 14, passes through screen 17a and through the catalyst bed in stage 14a. The vapor phase travels through stage 14a of reactor 14 and then to line 19a. Line 19a transports the vapors to mixing zone 16b of stage 14b. The vapor then travels through screen 17b and the catalyst bed in 14b, and then to line 19b. Line 19b transports the vapor to mixing zone 16c of stage 14c. The vapor is then passed through screen 17c and the catalyst bed of stage 14c, and then to line 19c, whereby the vapor is transported to mixing zone 16d of stage 14d. The vapor then passes through screen 17d and the catalyst bed of stage 14d. The vapor then is passed to line 19d and transported to mixing zone 16e of stage 14e. The vapors pass through screen 17e of stage 14e and through the catalyst bed of stage 14e. The vapors, after passing through the catalyst bed, are then withdrawn from reactor 14 through flexible line 20.

The passing of the vapor phase reactant through mixing zones 16a through 16e, screens 17a through 17e, and the catalyst beds of stages 14a through 14e, by means of line 13 and lines 19a through 19d, provides for a flow of the vapor phase reactant in a direction countercurrent to the flow of the solids, which flow from stage 14e to stage 14a of reactor 14. The catalyst in each stage of reactor 14 is a fluidized bed, with the fluidization caused by vibration of the reactor 14. In the embodiment shown, fresh catalyst is added to stage 14e of reactor 14, and the catalyst travels from stage 14e, and through stages 14d, 14c, 14b, and 14a, respectively. Thus the movement of the catalyst from compartment to compartment is countercurrent to that of the movement of the vapor phase, although it contemplated that the catalyst and vapor phase may move concurrently from compartment to compartment.

As the vapor phase is passed through stages 14a through 14e, the vapor phase is converted to a desired product, as it is passed through the fluidized beds of moving catalyst, which moves from stage 14e, through stages 14d, 14c, 14b, and 14a. As the catalyst is passed through these stages, it becomes inactivated, and may be withdrawn from reactor 14, and reactivated as hereinbelow described.

It is to be understood that the fluidization of the catalyst beds of the catalyst beds in stages 14a through 14e of reactor 14 is caused by the vibration of the reactor 14 by a vibrating means, and is independent of the velocity of the vapor phase passing over the catalyst beds 14a through 14e. Thus, one may pass the vapor or fluid phase over the fluidized catalyst beds for a time suffi-

cient to effect reaction or conversion of essentially the fluid phase reactant or reactants, thus minimizing or eliminating the necessity of recycling fluid phase reactants.

Although the embodiment shown depicts reactant being introduced into stage 14a and product withdrawn from stage 14e, it is also contemplated that the reactant or reactants may be added to each of stages 14a through 14e. It is also contemplated within the scope of the present invention that product may be recovered from each of stages 14a through 14e and that the remaining unreacted fluid phase portion be returned to the next successive stage or compartment.

The vapor phase, after being passed through the catalyst beds in stages 14a through 14e, is withdrawn as a desired vapor phase product through flexible line 20. Flexible line 20 is designed so as to absorb the shock of the vibration of reactor 14. The vapor phase product is then passed through line 21 to condenser 22, whereby the vapor product is condensed, and then withdrawn through line 23. The condensed vapors are then passed to separator 24, whereby liquid effluent product is recovered through line 25. Any remaining gases are withdrawn through line 27, and passed through compressor 27 to line 11, whereby the gases are fed along with a fresh feedstock to preheater 12. A portion of these gases may be shunted to gas bypass line 28 so as to avoid an excessive gas pressure in preheater 12, line 13, and reactor 14. The gas in line 28 then passes through flexible line 29, and then to catalyst withdrawal line 30.

After the solid catalyst particles have been passed to stage 14a, the catalyst, which has become inactivated as a result of its contact with the vapor phase reactants in stages 14e, 14d, 14c, 14b, and 14a, is withdrawn from reactor 14 through line 30, wherein the catalyst is contacted with gas passed from flexible line 29 as described above. The catalyst and gas are then passed through flexible line 31, line 32, and line 33, and fed to a single stage vertically oriented fluidized bed vessel 37. In fluidized bed vessel 37, the spent catalyst is heated by air which has been fed to preheater 35 through line 34, and withdrawn from preheater 35 through line 36. Preheater 35 is operated at a temperature of from about 150° C. to about 500° C. The heated air in line 36 is fed to fluidized bed vessel 37. The stream of air introduced to fluidized bed vessel 37 as well as any gas which may be in line 33, causes the fluidization of the catalyst particles.

The introduction of heated air from line 36 serves to reactivate the spent catalyst in fluidized bed vessel 37. The catalyst remains in fluidized bed vessel 37 for a period of time of from about 1 sec. to about 30 sec. In addition, fresh catalyst may be introduced to the fluidized bed vessel 37 through line 41. When heated to a temperature and for a time sufficient to reactivate the spent catalyst, the regenerated catalyst and fresh catalyst are withdrawn from the fluidized bed vessel 37 through line 38, passed through flexible line 39, and introduced into stage 14e of vibrating fluidized bed reactor 14, through line 40, wherein the catalyst will be contacted with a fluid phase reactant, and be passed along stages 14e, 14d, 14c, 14b, and 14a of reactor 14.

Air and other gases within fluidized bed vessel 37 may be withdrawn from vessel 37 through line 42. Line 42 may also contain a small portion of catalyst. The gas in line 42 is passed to cyclone 44. Catalyst fines are recovered from cyclone 44 through line 45, and the gas is withdrawn from cyclone 44 through line 46, and

passed through pump 47. A portion of the gas is vented through line 48, and another portion may be passed to line 33 where it joins spent catalyst passed from line 32, and is returned to fluidized bed vessel 37.

In FIG. 2 is depicted an embodiment wherein oxygen is fed to each stage of a multi-stage vibrating fluidized bed reactor for carrying out an oxidation reaction. A fluid phase feedstock, which may be a liquid or vapor phase, in line 110 is heated in preheater 112, and passed to line 113. The feedstock then is admixed with air or oxygen in flexible line 109, said air or oxygen being passed to flexible line 109 from line 108. The feed, as well as the air or oxygen, is then introduced to distributor 116a of stage 114a of reactor 114. Reactor 114 is a multi-stage vibrating fluidized bed reactor, comprised of stages 114a through 114d. Although four stages, 114a through 114d of reactor 114 are shown, it is contemplated that reactor 114 may contain any number of stages, as long as at least two stages are present.

Reactor 114 also includes mixing zones 116a through 116d, constructed as hereinabove described for mixing zones 16a through 16e in FIG. 1, and screens 117a through 117d. A catalyst bed lies above each of screens 117a through 117d. Partitions 118a through 118c divide the reactor into stages 114a through 114d. Also attached to reactor 114 are springs 115a and 115b, which are connected to a vibrating means (not shown).

The catalyst beds in each of stages 114a through 114d are fluidized beds. The fluidization of the beds is caused by the vibration of the reactor 114 by the vibrating means. In the embodiment shown, the catalyst moves from stage 114d to stage 114a, or countercurrent to the movement of the fluid phase reactants.

The feedstock and the air or oxygen, introduced into mixing zone 116a, passes through screen 117a and through the catalyst bed in stage 114a. The reactants, plus any product which may be formed, are then passed to line 119a, which transports the fluid, or vapor phase to mixing zone 116b. The fluid, or vapor phase, therefore is passed through lines 119a, 119b, and 119c, and through mixing zones 116a through 116d and stages 114a through 114d so as to achieve a flow of the fluid, or vapor phase which is countercurrent to the flow of the catalyst.

Make-up oxygen in line 101 is passed to flexible line 102, and then to line 103. The make-up oxygen is then passed to line 103a, whereby the oxygen is combined with fluid phase reactants and/or product in line 119a, to line 103b, whereby the oxygen is passed to a fluid phase in line 119b, and to line 103c, whereby the oxygen is passed to a fluid phase in line 119c. In this way, make-up oxygen is added, along with fluid phase reactants and/or product, to each of mixing zones 116b, 116c, and 116d, thus enabling make-up oxygen to be fed to each of stages 114b through 114d, which enables one to maintain a desired concentration of oxygen in each of the stages of reactor 114.

Product in stage 114d of reactor 114 is withdrawn through flexible line 120, and passed through line 121 to condenser 122. The effluent is then passed through line 123 to vapor-liquid separator 124. A liquid effluent product is recovered through line 125, while vapors are withdrawn through line 126. A portion of the vapors is vented through line 128, while the rest of the vapors are passed through compressor 127 and line 129, to be joined with fresh feedstock in line 113.

The catalyst, which has been passed from stages 114d to 114a, becomes inactivated as it has been passed coun-

tercurrently to the movement of the fluid phase reactants. Spent catalyst in stage 214a is withdrawn through lines 130 and 131 and passed to a catalyst regeneration zone (not shown). The catalyst may be regenerated as hereinabove described.

Referring now to FIG. 3, which depicts a co-polymerization of propylene with ethylene or butylene, a gaseous or vapor phase stream of propylene is passed through line 210, combined with recycle propylene and/or ethylene or butylene in line 237, and then passed through line 211, flexible line 212, and line 213, to mixing zone 216 of multistage vibrating fluidized bed reactor 214. Mixing zone 216 serves to distribute the fresh or recycle propylene, as well as fresh or recycle ethylene or butylene, evenly under the catalyst beds in each of stages 214a through 214d of reactor 214. A solid catalyst dispersed in a liquid is also introduced into stage 214a of reactor 214 from line 220, flexible line 221, and line 222. As the dispersion is introduced, the liquid evaporates and the solid catalyst is deposited upon the growing particles of solid polymer lying upon screen 217a in stage 214a. The catalyst is then passed through stages 214a through 214d through vibration of reactor 214.

Multistage vibrating fluidized bed reactor 214 is comprised of stages 214a, 214b, 214c, and 214d, and is disposed at an incline so as to aid in the flow of solid polymer product, containing the trace amount of catalyst, from stage 214a to stage 214d. Reactor 214 is operated under polymerization conditions as hereinabove described. The reactor is also connected to a vibrating means (not shown), which moves springs 215a and 215b, thereby causing vibration of the reactor. Although four stages 214a through 214d of the reactor are shown, the number of stages or compartments may vary as long as at least two stages or compartments are present.

Contained within reactor 214 are partitioning means 218a, 218b, and 218c, which separate the reactor 214 into the stages or compartments 214a, 214b, 214c, and 214d. A mixing zone 216 is located at the bottom of reactor 214. Located above distributor 216 are screens 217a through 217d, upon each of which lies a bed of polymer particles, or beads, containing the catalyst. The polymer particles, formed by the vapor phase polymerization of olefins (ethylene, propylene, 1-butene, etc.) on the surface of the catalyst particles, which are continuously growing, as the polymerization reaction takes place. Attached to reactor 214 are springs 215a and 215b, which are attached to a vibrating means (not shown), which causes vibration of the reactor and fluidization of the solids in stages 214a through 214d. Also disposed across the width of reactor 214 are baffles 219a, 219b, and 219c. As the reactor 214 is vibrated, the solids travel from stage 214a, over baffle 219a, through stage 214b, over baffle 219b, through stage 214c, over baffle 219c through stage 214d. As the solids are passed over baffles 219a, 219b, and 219c, the flowing solids between baffles 219a, 219b, and 219c and partitions 218a, 218b, and 218c, provides for a seal of each of stages 214 through 214d, which prevents the passage of reactant gases between stages of reactor 214.

Mixing zone 216 enables the propylene, plus any recycle ethylene or butylene, to be distributed evenly below each of stages 214a through 214d of reactor 214. The propylene plus the recycle gases is thus simultaneously introduced through screens 217a through 217d,

and through the catalyst beds in stages 214a through 214d.

Fresh ethylene or butylene vapors in line 223 are also passed through flexible line 224, and into lines 225a, 225b, and 225c, and are then passed to mixing zone 216. Line 225a is aligned under the solids bed of stage 214b, line 225b is aligned under the solids bed in stage 214c, and line 225c is aligned under the solids bed of stage 214d. The introduction of fresh butylene or ethylene from lines 225a, 225b, and 225c into mixing zone 216 thus enables for an even distribution of ethylene or butylene under the solids beds of stages 214a through 214d. As the ethylene or butylene, and the propylene, come into contact with each other in each of the separate stages 214a through 214d in reactor 214 in the presence of the catalyst, a solid copolymer of propylene with ethylene or butylene begins to form. As the solid copolymer product is formed, it is deposited in the catalyst beds of each of stages 214a through 214d of reactor 214, and is passed from stage to stage of reactor 214, along with the catalyst. The amount of solid copolymer product increases as the solids are passed through the stages 214a through 214d of reactor 214, and as propylene and ethylene or butylene are reacted separately in each stage so as to form the solid copolymer.

As stated above, the movement of catalyst and/or solid polymer product over baffles 219a through 219c, as the solids are passed from stages 214a through 214d, seals each of stages 214a through 214d such that no gaseous reactants are passed between the stages 214a through 214d. Thus, there is provided a cross-current flow of the propylene and ethylene or butylene vapors against the movement of the solids in each of stages 214a through 214d.

It is also to be understood that the catalyst beds in stages 214a through 214d of reactor 214 are fluidized by the vibration of a vibrating means, and that the fluidization of the catalyst beds, as well as the solid polymer which becomes admixed with the catalyst as the reaction progresses, is independent of the velocity of the propylene and butylene or ethylene vapors which pass over the catalyst beds in stages 214a through 214d. Thus, the propylene and ethylene or butylene vapors may be passed over the fluidized catalyst beds for a time sufficient to effect reaction of the propylene with the ethylene or butylene to form a copolymer. This minimizes the amount of vapors which need to be recycled to the multistage vibrating fluidized bed reactor 214.

The solid copolymer product, upon being deposited in or passed to stage 214d, is withdrawn along with the solid catalyst from stage 214d of reactor 214 through line 230. A stream of inert gas is also passed to line 230 from line 238 and flexible line 239. Because, as hereinabove stated, a small amount of polymerization catalyst is necessary in such a polymerization process, it is not necessary to separate the solid polymer from the catalyst, nor is it necessary to regenerate such a small amount of catalyst. The solid polymer in line 230 is then passed through flexible line 231 and recovered through line 232.

Unreacted propylene and/or ethylene or butylene vapors, in each of stages 214a through 214d are withdrawn separately from stages 214a, 214b, 214c, and 214d of reactor 214 through lines 226a, 226b, 226c, and 226d, respectively. The unreacted vapors in lines 226a through 226d are passed to line 227, and then passed through flexible line 228 and line 229. The unreacted

vapors are then passed through compressor 233. A portion of the unreacted vapor phase is vented through line 235, whereas another portion is passed through line 234 through cooler 236, and line 237. The cooled vapors are combined with fresh propylene from line 210 in line 211, whereby the vapors are fed to mixing zone 216 of reactor 214.

Advantages of the present invention include the ability to effect fluidization of the solid catalyst beds independently of the flow rate or velocity of the fluid phase which is passed over the catalyst beds. This enables one to keep the reactant or reactants in contact with the solid catalyst particles for a period of time sufficient to effect a conversion of reactants to a desired product and minimizing the amount of reactants which need to be recycled. The partitioning of the reactor into at least two stages enables one, if desired, to add a portion of one or more reactants to each stage. This also increases the chances of reacting all of the reactant feed and minimizes the amount of feed that is recycled to the reactor. The staging of the reactor, whereby a portion of one or more reactants is added to each stage, allows the adjustment of the ratio of reactants or comonomers for each stage independently, thereby achieving the optimum concentration profile (as desired, depending on the nature of the reaction) throughout the multistage reactor. It is particularly advantageous when employed in conjunction with highly exothermic reactions which have an unstable product or intermediate, and wherein the intermediate is the desired product. The addition of a portion of one or more reactants to each stage enables one to increase the selectivity of the reaction for a desired product.

It is to be understood that the scope of the present invention is not to be limited to the specific embodiments described above. The invention may be practiced

other than as particularly described and still be within the scope of the accompanying claims.

What is claimed is:

1. A process for reacting a gas phase with a solid phase in a multistage fluidized bed vessel including at least first and second compartments, comprising:

maintaining a fluidized bed of solids of said solid phase in each compartment by vibrating said vessel and passing said gas phase upwardly through the solids in each compartment, and wherein at least a portion of said gas phase is introduced after passage through said first compartment to a second compartment below the fluidized bed in said second compartment; and continuously passing solids from one compartment to another compartment in essentially plug flow, said solids in passing from one compartment to another compartment providing a gas seal between said compartments to prevent the passage of said gas phase between said compartments.

2. The process of claim 1 wherein said vessel includes at least one vertical baffle, said at least one vertical baffle dividing said vessel into at least two compartments and extending downwardly from the top of said vessel and spaced from the bottom of said vessel, thereby providing for at least one space between said at least one vertical baffle and the bottom of said vessel and passing solids from one compartment to another compartment through said space.

3. The process of claim 1 wherein said gas phase moves through each compartment counter-currently with the direction of movement of said solids.

4. The process of claim 1 wherein said solid phase is comprised of a catalyst.

5. The process of claim 4 wherein said solid phase further comprises a solid reaction product.

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